

**Structural Characterization of Uranium Complexed to Naturally Occurring Organics**

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Beamline X11A

**Introduction:** Radionuclides have been disposed of in subsurface environments at DOE nuclear processing facilities. The presence of complexing agents in the subsurface increase the transport of radionuclides from these sites. An understanding of the nature of the metal-ligand association can lead to development of innovative treatment methods to decrease contaminant mobility.

**Methods and Materials:** Structural characterization of uranium complexed with naturally occurring malic and citric acids, and catechol, a humate-like dihydroxyphenol compound, was performed using extended X-ray absorption fine structure analysis (EXAFS). The 1:1 U:catechol (50 mM, pH 4.8), 1:1 U:malic acid (50 mM, pH 6.1), and 1:1 U:citric acid (100 mM, pH 6.1) complexes were prepared by addition of uranyl nitrate to an aqueous solution of the ligand. The pH was adjusted, the sample was placed in a heat-sealed polypropylene bag, and analysis was performed at the U  $L_{III}$  edge (17.166 keV) in the transmission mode. Backscattering phase and amplitude information for individual neighboring atoms was obtained using the theoretical modeling code FEFF 7.02.

**Results:** Figure 1A shows the raw  $k^3$ -weighted spectra and the fitting results for U-catechol (2.8-13.4  $\text{\AA}^{-1}$ ), U-malic acid (2.8-13.4  $\text{\AA}^{-1}$ ), and U-citric acid (3.7-15.0  $\text{\AA}^{-1}$ ). The complexes have distinct amplitude and oscillation features indicating the nature of the ligand bonding to uranium. Figure 1B shows the Fourier transform and the results of the fitting for each U-ligand complex. The peaks in the transform represent coordination shells at radial distances from the uranium atom. The near-neighbor environment for U-catechol consists of 2.0 axial oxygen (O) atoms at 1.77  $\text{\AA}$ , 4.9 equatorial Os at 2.36  $\text{\AA}$ , 2.0 carbon (C) atoms at 2.90  $\text{\AA}$ , and a U-U interaction at 4.03  $\text{\AA}$ . The U-malate complex has 2.0 axial Os at 1.81  $\text{\AA}$ , 5.1 equatorial Os at 2.37  $\text{\AA}$ , 2.0 Cs at 2.93  $\text{\AA}$ , and a U-U interaction at 4.08  $\text{\AA}$ . The near-neighbor atoms for U-citrate complex includes 2.3 axial Os at 1.79  $\text{\AA}$ , a split equatorial shell consisting of 4.0 Os at 2.32  $\text{\AA}$  and 1.0 O's at 2.47  $\text{\AA}$ , 2.0 Cs at 2.93  $\text{\AA}$ , and a U-U interaction at 3.78  $\text{\AA}$ . The proposed structures for the complexes are presented in Figure 2.

**Conclusions:** Uranium forms binuclear complexes with catechol, malic acid, and citric acid. The uranium atoms are bonded through  $\mu_2$ -OH groups. The catechol was bonded to uranium through the two hydroxyl groups and the hydroxycarboxylic acids were bonded in tridentate fashion to uranium through two carboxylate and the hydroxyl functional groups.

**References:** 1. Dodge, C.J.; Francis, A.J. 1997. Environ. Sci. Technol. 31:3062.

2. Dodge, C.J. 1999. Ph.D. dissertation, SUNY-Stony Brook.

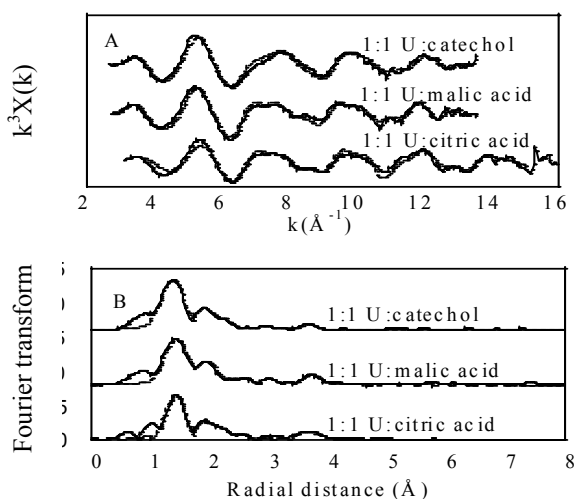


Figure 1. EXAFS data for equimolar U-catechol, U-malate, and U-citrate complexes. Experimental data (—); fitted data (---).

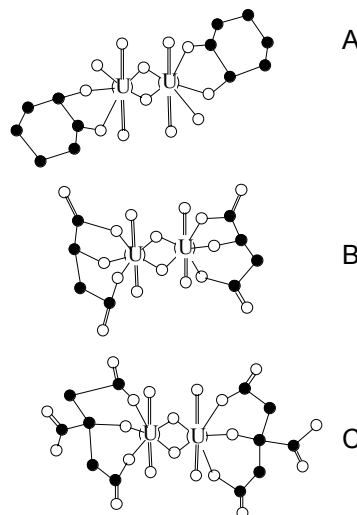


Figure 2. Proposed structures for U-catechol (A), U-malate (B), and U-citrate (C) complexes.